(51) International Patent Classification:
C08G 12/00 (2006.01)
(21) International Application Number:
PCT/EP20 13/075472
(22) International Filing Date:
4 December 2013 (04.12.2013)
(25) Filing Language:
English
(26) Publication Language:
English
(30) Priority Data:
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Published: 
— with effect from publication to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: (METH)ACRYLATED AMINO RESINS
(57) Abstract: The present invention relates to amino resins bearing (meth)acrylic groups, to processes for preparing them, to their use, and to coating compositions comprising them.
(Meth)acrylated amino resins

Description

The present invention relates to amino resins bearing (meth)acrylic groups, to processes for preparing them, to their use, and to coating compositions comprising them.

Pigmented paints and transparent varnishes comprising or based on melamine-formaldehyde resins have been known for a number of decades.

Unplasticized melamine-formaldehyde resins serve, either on their own or in combination with further, chemically different crosslinkers, examples being blocked polyisocyanates, trisalkylcarbamoyltriazines (TACT) or epoxides, as a crosslinking component in binder mixtures. Curing of the film-forming constituents produces a coating which is resistant to chemical, mechanical, and weathering-induced influences. Plasticized melamine-formaldehyde resins may feature modifications with carbamate structures, blends with polyesters or alkyd resins, and/or precondensations with the latter. When used on flexible coating substrates lacking dimensional stability, unplasticized melamine-formaldehyde resins require external elastification in order for the coating not to tear; as a sole formulating constituent, the crosslinker forms only brittle networks.

Melamine-formaldehyde resins can be characterized according to application (molding compounds, glues, impregnating resins, coating materials), alkylating compounds (etherification with butanol, methanol, mixed etherification) or, as set out here, by the ratio of triazine to formaldehyde to etherifying alcohol:

1. fully to highly methylolated and fully alkylated resins (HMMM grades)
2. partly methylolated and highly alkylated resins (high imino grades)
3. partly methylolated and partly alkylated resins (methylol grades)
4. resins with a low degree of methylolation (melamine-formaldehyde condensates)

The first major group of the fully etherified melamine-formaldehyde resins, in which the molar melamine:formaldehyde:alcohol incorporation ratio is theoretically 1:6:6, in practice generally 1:5.5:5.0, and usually 1:5.5:4.0, is distinguished by extremely good high-solids behavior (relatively low viscosity at high solids content). In this group of crosslinkers the free formaldehyde is readily reducible. At the present time it is possible to achieve a free formaldehyde content < 0.3% by weight. The commercial products usually comprise methanol as the alcohol, although grades with mixed etherification, and fully butylated grades, are also known.

The fully etherified melamine-formaldehyde resins are employed in practice preferably in can coating and coil coating and for all coats of the automobile finish.

The low thermal reactivity under baking conditions, such as 20 minutes at 140°C, necessitates catalysis with strong acids for these fully etherified melamine-formaldehyde resins. This results in very rapid curing, and a homogeneous co-network as a result of transetherification with the
binder, accompanied by the release of the etherifying alcohols. With this strong-acid catalysis, very short cure times are possible, as in the case of partly methylolated melamine-formaldehyde resins. Crosslinking may be accompanied by formaldehyde emission which goes well beyond the free formaldehyde and is due to the re-cleavage of methylol groups.

The second major group of the partly etherified melamine-formaldehyde resins, which in practice generally feature a molar melamine:formaldehyde:alcohol incorporation ratio of 1:3 to 5.4:2 to 4.3, is distinguished by a thermal reactivity which is significantly increased in comparison to the first group, without acid catalysis. The production of these crosslinkers is accompanied by self-condensation, leading to a higher viscosity (lower high-solids behavior) and making the removal of the free formaldehyde during distillation more difficult as a result. For these products a free formaldehyde content of 0.5% to 1.5% is standard, though there are also products having a free formaldehyde content of 0.3% to 3% by weight. Here again, methylated and butylated commercial products, and also grades with mixed etherification, are widespread. Etherification with other alkylating compounds is described in the literature, and the corresponding products are available as specialty products.

High-imino grades and methylol grades, each as a subgroup, both feature incomplete methylation, i.e., molar formaldehyde incorporation ratios of less than 1:5.5. The high-imino grades differ from the methylol grades, however, in a high degree of alkylation, i.e., in the proportion of the etherified methylol groups as a fraction of the incorporated formaldehyde equivalents, which is usually up to 80%, whereas for the methylol grades it is generally < 70%.

Applications for the partly methylolated melamine-formaldehyde resins extend across all fields of use, including combinations with HMMM grades, for adaptation of reactivity, where curing temperatures of 100 to 150°C are required. Additional catalysis using weak acids is possible and is common practice.

Besides the reaction of the amino resin with the binder there is a substantially increased proportion of self-crosslinking on the part of the crosslinker. The consequence is reduced elasticity in the system as a whole, and this reduction must be compensated by an appropriate selection of the co-component. Set against this is the advantage of reduced total formaldehyde emission from the coatings produced from the system.

Finishes based on melamine-formaldehyde condensation resins are used in the automotive segment, for industrial coatings generally, but also for wood and plastic. The coating systems feature particular hardness, gloss, resistance to chemicals and to yellowing, and weather resistance.

Their structural flexibility makes melamine-formaldehyde resins interesting starting compounds for radiation-curable compounds.
Reaction products of etherified melamines with hydroxyl acrylates are known for application in radiation-curable coating compositions; see, for example, T. J. Giacobbe et al., Macromolecules, 4, 1971, 630 ff. or JP63286426.

The presence of acid-labile formals or N,O-acetals, however, makes such structures unstable in the acidic pH range, and this is manifested, for example, in lability under moisture exposure (see below).

US 4,266,053 describes (meth)acrylates comprising melamine rings, prepared as reaction products of melamine-based polyols with (meth)acrylic acid, for use in UV-curing coatings on among others - plastics parts. Although they feature better moisture resistance than the compounds described by T. J. Giacobbe et al. (see comparative example 1 in table 1 of US 4,266,053), their preparation is necessarily complicated, on the basis of cyanuric chloride.

WO 201 1/015539 discloses radiation-curable compounds obtainable by reacting at least one melamine-formaldehyde resin with at least one carbamato (meth)acrylate.

However, such a carbamato (meth)acrylate is to be prepared from an carbamato alcohol by esterification or transesterification with (meth)acrylic acid or with a (meth)acrylic ester.

It is a disadvantage to prepare the carbamato (meth)acrylate and the carbamato alcohol via several steps.

It was an object of the present invention to provide new, radiation-curable compounds based on melamine-formaldehyde resins that are stable to re-cleavage over a broad pH range, and are simple to prepare.

The invention relates to a process for the preparation of (meth)acrylated melamine-formaldehyde resins, wherein at least one at least one partially methylolated melamine-formaldehyde resin of formula (I)
wherein

$\mathbf{R}^1, \mathbf{R}^2, \mathbf{R}^3, \mathbf{R}^4, \mathbf{R}^5$ und $\mathbf{R}^6$ are each independently of another a $\text{C}_1$- to $\text{C}_2$-alkyl radical and

$k, m, n, o, p$ und $q$ are each independently of another a positive integer of 1 to 10

is reacted with (meth)acrylic acid in the presence of at least one acid (B) yielding a
(meth)acrylated melamine-formaldehyde resin of formula (II)

wherein

$\mathbf{R}^7, \mathbf{R}^8, \mathbf{R}^9, \mathbf{R}^{10}, \mathbf{R}^{11}$ und $\mathbf{R}^{12}$ are each independently of another a $\text{C}_1$- to $\text{C}_2$-alkyl residue or a
(meth)acryloyl group and

$r, s, t, u, v,$ and $w$ are each independently of another 0 (zero) or a positive integer of 1 to 10,
wherein at least one of \( r, s, t, u, v, \) and \( w \) is \( > 0 \) (zero),
with the proviso that at least three of the radicals \( R^7 \) to \( R^{12} \) are (meth)acryloyl
groups.

\[ R^1 \text{ to } R^6 \text{ and } R^7 \text{ to } R^{12} \text{ are independently of each other } \text{Ci- to } C_{20}-\text{alkyl, preferably } \text{Ci to } C_4 \text{ alkyl,}
more preferably methyl, ethyl, isobutyl or n-butyl, very preferably methyl or n-butyl, and especially methyl.

\text{Ci- to } C_{20}-\text{alkyl in the context of the present specification refers to straight-chain or branched}
alkyl groups having one to 20 carbon atoms, preferably Ci-Cs alkyl groups, i.e., for example,
methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, 2-butyl, tert-butyl, 1-pentyl, 2-pentyl, isoamyl,
n-hexyl, n-octyl or 2-ethylhexyl.

\text{Ci-C}_4 \text{ alkyl refers in this specification to methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl,}
2-butyl, or tert-butyl.

\[ k, m, n, o, p \text{ and } q \text{ are each independently of another a positive integer of } 1 \text{ to } 10.

\[ r, s, t, u, v, \text{ and } w \text{ are each independently of another } 0 \text{ (zero) or a positive integer of } 1 \text{ to } 10,
wherein at least one of \( r, s, t, u, v, \) and \( w \) is \( > 0 \) (zero), with the proviso that \( r \leq k, s \leq m, t \leq n, u \leq o, v \leq p, \text{ and } w \leq q.

The amino resins (A) may preferably be melamine-formaldehyde resins of formula (I) and
benzoguanamine/formaldehyde resins of formula (III) (see below), each of which may optionally
be at least partly etherified, and which preferably are at least partly etherified.

The resins more preferably are at least partly etherified melamine-formaldehyde resins or
benzoguanamine/formaldehyde resins, and very preferably are at least partly etherified
melamine-formaldehyde resins.

The structure of melamine-formaldehyde resins which can be employed as amino resins (A) in
accordance with the invention is, for example, as follows:

As mentioned earlier, melamine-formaldehyde resins are frequently characterized by way of the
molar melamine : formaldehyde : alcohol incorporation ratio. The alcohol here equates to
alcanols of the formula \( R^1 \text{OH}, R^2 \text{OH}, R^3 \text{OH}, R^4 \text{OH}, R^5 \text{OH}, \text{ and } R^6 \text{OH}, \) and is preferably selected
from the group consisting of methanol, ethanol, isobutanol and n-butanol or mixtures thereof,
and more preferably selected from the group consisting of methanol and n-butanol.

Melamine-formaldehyde resins which can be used in accordance with the invention may have a
molar incorporation ratio of 1:2 to 6:1 to 6, though in individual cases, as a result of the
formation of oligoformal chains, the formaldehyde incorporation ratio may even be up to 8.
Preferred molar incorporation ratios are 1:3 to 6:1.5 to 6.
For methyl-etherified melamine-formaldehyde resins, molar incorporation ratios of 1:3.6 to 5.7:2.1 to 4.7 are particularly preferred; very much preferred are molar incorporation ratios of 1:5 to 6:3.5 to 6, more particularly 1:5 to 6:4.0 to 5.0.

For n-butyl-etherified melamine-formaldehyde resins, molar incorporation ratios of 1:3.2 to 5.7:1.3 to 4 are particularly preferred; very much preferred are molar incorporation ratios of 1:5 to 6:3.5 to 6, more particularly 1:5 to 6:3.5 to 4.5.

The melamine-formaldehyde resins that can be used may have not only one melamine group per polycondensate but, indeed, two or more melamine groups, preferably up to six, more preferably up to four, very preferably up to three, and more particularly up to two.

The structure of benzoguanamine/formaldehyde resins which can be used as amino resins in accordance with the invention is, for example, as follows (formula (III)):

\[
\begin{align*}
\text{R}^1 & \quad \text{O} \quad \text{O} \quad \text{R}^2 \\
\text{N} & \quad \text{N} \\
\text{R}^3 & \quad \text{O} \\
\text{R}^4 & \quad \text{O} \\
\text{R} & 
\end{align*}
\]

wherein

\[ R^1, R^2, R^3 \text{ and } R^4 \text{ are each independently of another a } \text{C}1- \text{ to C}2- \text{alkyl radical and } \]

\[ k, m, n, \text{ and } o \text{ are each independently of another a positive integer of 1 to 10.} \]

The reaction product in this case is of formula (IV)
wherein

\[ R^7, R^8, R^9 \text{ and } R^{10} \text{ are each independently of another a } \text{Cl}_i \text{- to } \text{Cl}_2 \text{-alkyl residue or a } (\text{meth})\text{acryloyl group and } \\
\text{r, s, t, and u are each independently of another 0 (zero) or a positive integer of 1 to 10, wherein at least one of r, s, t, and u is } > 0 \text{ (zero), with the proviso that at least two of the radicals } R^7 \text{ to } R^{12} \text{ are (meth)acryloyl group.} \]

Benzoguanamine-formaldehyde resins as well are frequently characterized by way of the molar benzoguanamine:formaldehyde:alcohol incorporation ratio. The alcohol in this case is preferably selected from the group consisting of methanol, ethanol, isobutanol and n-butanol or mixtures thereof, more preferably selected from the group consisting of methanol and n-butanol.

Benzoguanamine-formaldehyde resins which can be used in accordance with the invention may have a molar incorporation ratio of 1:1.5 to 4:1 to 4, though in certain cases, as a result of formation of oligoformal chains, the formaldehyde incorporation ratio may even be up to 6.

Preference is given to molar incorporation ratios of 1:2 to 4:1.5 to 4.

For methyl-etherified benzoguanamine-formaldehyde resins, molar incorporation ratios of 1:2.2 to 3.7:2.1 to 3.0 are particularly preferred; very particular preference is given to molar incorporation ratios of 1:3 to 4:1.5 to 4, more particularly 1:3 to 4:2.0 to 3.0.

For n-butyl-etherified benzoguanamine-formaldehyde resins, molar incorporation ratios of 1:2.2 to 3.7:1.3 to 2 are particularly preferred; very particular preference is given to molar incorporation ratios of 1:3 to 4:1.5 to 4, more particularly 1:3 to 4:1.5 to 2.5.
The benzoguanamine-formaldehyde resins which can be used may have not only one benzoguanamine group per polycondensate but also, indeed, two or more benzoguanamine groups, preferably up to five, more preferably up to four, very preferably up to three, and more particularly up to two.

The amino resin used may comprise at least one solvent, such as water or alcohols.

Alcohols are for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, pentanol isomer mixtures, hexanol isomer mixtures, 2-ethylhexanol or octanol.

Preferred solvents are water or C1-C4 alkyl alcohols, as for example, methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, sec-butanol or tert-butanol, or aromatic hydrocarbons, such as toluene or xylene isomer mixtures, for example.

The free formaldehyde content of the amino resin used is generally not more than 1.5% by weight; for example, it may be not more than 1.0%, preferably not more than 0.5%, more preferably not more than 0.3%, and very preferably not more than 0.1% by weight.

In the reaction according to the invention the amino resin is reacted with (meth)acrylic acid, preferably with acrylic acid.

The reaction to form the (meth)acrylated amino resins of the invention may take place between 40 and 120°C, more preferably between 60 and 110°C, and very preferably between 70 and 100°C for 1 to 12 hours, preferably 2 to 10 hours. In a preferred embodiment the reaction is conducted under reduced pressure, preferably from 10 to 700, very preferably from 15 to 500 and especially preferably from 20 to 300 hPa, so that alcohol R1OH to R6OH which is released during the reaction is distilled off.

The reaction can be carried out in bulk, but is preferably carried out in an inert, anhydrous solvent.

The reaction of the amino resin used with (meth)acrylic acid may take place in the presence of an acid (B) and with or without addition of an azeotrope former, such as toluene. As a catalyst an acid (B) is used. Examples of acids are given below.

Depending on the desired degree of substitution, (meth)acrylic acid is used in a ratio of 1:1 to 20:1 (molar) with respect to amino resin, preferably in a ratio of 6:6 to 15:6, particularly preferably in a ratio of approximately 10:6. The excess (meth)acrylic acid is removed from the reaction mixture after the end of the reaction, under reduced pressure and at not more than 50°C.

Further heating of the reaction mixture may lead to the polymerization of the amino resin.

One preferred embodiment of the present invention involves selecting the ratio of (meth)acrylic acid to amino resin (A) such that the resultant resin has an average degree of substitution with
(meth)acryloyl groups per melamine nucleus of at least three, preferably three to five, very preferably three to 4.5 and especially preferably three to four.

During this reaction it is possible, though less preferred, for there to be a condensation of the amino resins to form polynuclear melamine-formaldehyde condensates or benzoguanamine condensates. In this case, amino resins which are polynuclear or have a higher number of nuclei are synthesized.

Therefore, for the reaction of the amino resin with (meth)acrylic acid it would also be conceivable to apply a subatmospheric pressure in order to reduce the temperature. This would reduce the self-condensation of the amino resins and would lead to smaller molecules with a lower viscosity. Conversely, in order to synthesize polynuclear amino resins, it would be possible to prolong the running time of the reaction and/or to carry it out at an elevated temperature.

The alcohol, preferably methanol liberated is collected continuously in a water separator and the reaction is terminated when the theoretical amount of methanol has been separated off. If water is present in the reaction mixture, it is advantageous to use a short Vigreux column for effective separation of the azeotrope, comprising (meth)acrylic acid and water, from the alcohol, preferably methanol formed. Preferably, however, the reaction is carried out in the absence of water.

Suitable acidic catalysts (B) exhibit a pKa-value of 3 or less, preferably 2.5 or less. Preferred acids are sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, para-toluensulfonic acid, benzenesulfonic acid, dodecylbenzenesulfonic acid, methanesulfonic acid, nonylnapthalenedisulfonic acid or mixtures thereof; acidic ion exchangers can also be contemplated. Particular preference is given to sulfonic acids, particular preference to para-toluensulfonic acid.

The acidic catalyst (B) is added generally in amounts of 0.1 % to 1% by weight, preferably 0.1 % to 0.5% by weight. It may be useful to introduce the catalyst in a number of portions.

The number-average molar weight $M_n$ of the (meth)acrylated amino resins obtained, especially melamine-formaldehyde resins, is generally less than 3500 g/mol, preferably less than 3000 g/mol, and more preferably less than 2500 (as determined by gel permeation chromatography using tetrahydrofuran and polystyrene as standard, DIN 55672, part 1).

In one preferred embodiment the acid number of the amino resins obtained, especially the melamine-formaldehyde resins, is less than 80, more preferably less than 60 mg KOH/g and very preferably less than 50 mg KOH/g, as determined in accordance with ISO 3682. The acid number may be further reduced by separating off unreacted (meth)acrylic acid from the reaction mixture.
The free formaldehyde content of the (meth)acrylated amino resins of the invention is generally not more than 0.2% by weight, preferably not more than 0.15% by weight, and more preferably not more than 0.1% by weight.

5 The free formaldehyde content is determined in accordance with EN ISO 9020.

Another aspect of the present invention is a coating composition, comprising
- at least one (meth)acrylated melamine-formaldehyde resin, obtainable as described above,
- at least one binder (C), comprising groups that are reactive towards amino resins,
- optional at least one radiation curable compound (D),
- at least one photoinitiator (E),
- optional at least one pigment (F), and
- optional at least one typical coating additive (G).

15 Typically such a coating composition comprises

- 30 to 90, preferably 40 to 80% by weight of at least one (meth)acrylated melamine-formaldehyde resin, obtainable as described above,
- 10 to 50, preferably 20 to 40% by weight of at least one binder (C), comprising groups that are reactive towards amino resins,
- 0 to 50, preferably 5 to 40 and more preferably 10 to 30% by weight of at least one radiation curable compound (D),
- 0.1 to 5% by weight of at least one photoinitiator (E), and/or 0.1 to 10% by weight of an acid, preferably a strong acid,

25 - 0 to 30% by weight of at least one pigment (F), and
- 0 to 15% by weight of at least one typical coating additive (G),

with the proviso that the sum of the compounds always adds up to 100% by weight.

30 As binders (C), coating compositions of this kind comprise at least one binder comprising groups that are reactive toward amino resins. These are, generally, selected from the group consisting of epoxy-containing binders, hydroxyl-containing binders, carboxyl-containing binders, and amino-containing binders.

35 The hydroxyl-containing binder preferably comprises polyetherols, polyesterols, polyacrylate polyols, polycarbonate polyols, alkyd resins or epoxy resins. Polyesterols and polyacrylate polyols are particularly preferred, very particular preference being given to polyacrylate polyols.

The binders have on average per molecule at least two, preferably two to ten, more preferably three to ten, and very preferably three to eight hydroxyl groups.

40 The OH number, measured to DIN 53240-2, is generally from 10 to 200 mg KOH/g, preferably from 30 to 140.
The binders may additionally have an acid number to DIN EN ISO 3682 of 0 to 200 mg KOH/g, preferably 0 - 100, and more preferably 0 to 10 mg KOH/g.

The polyacrylate polyols are, for example, those which are copolymers of (meth)acrylic esters with at least one compound having at least one, preferably precisely one, hydroxyl group and at least one, preferably precisely one, (meth)acrylate group.

The latter may be, for example, monoesters of α,β-unsaturated carboxylic acids, such as acrylic acid, methacrylic acid (referred to in this text for short as "(meth)acrylic acid"), with diols or polyols which have preferably 2 to 20 carbon atoms and at least two hydroxyl groups, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,1-dimethyl-1,2-ethanediol, dipropylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, tripropylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, neopentyl glycol hydroxypivalate, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 1,6-hexanediol, 2-methyl-1,5-pentanediol, 2-ethyl-1,4-butanediol, 2-ethyl-1,3-hexanediol, 2,4-diethyloctane-1,3-diol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3-, and 1,4-bis(hydroxymethyl)cyclohexane, 1,2-, 1,3- or 1,4-cyclohexanediol, glycerol, trimethylolpropane, trimethylolbutane, pentaerythritol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol, isomalt, poly-THF having a molar weight between 162 and 2000, poly-1,3-propanediol or polypropylene glycol having a molar weight between 134 and 2000, or polyethylene glycol having a molar weight between 238 and 2000.

Preference is given to 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 1,4-butanediol monoacrylate or 3-(acryloyloxy)-2-hydroxypropyl acrylate, and particular preference to 2-hydroxyethyl acrylate and/or 2-hydroxyethyl methacrylate.

The hydroxyl-bearing monomers are employed in the copolymerization in mixture with other polymerizable, preferably free-radically polymerizable, monomers, preferably those composed of more than 50% by weight of C1-C20 alkyl (meth)acrylate, vinylaromatics having up to 20 carbon atoms, vinyl esters of carboxylic acids comprising up to 20 carbon atoms, vinyl halides, nonaromatic hydrocarbons having 4 to 8 carbon atoms and 1 or 2 double bonds, unsaturated nitriles, and mixtures thereof. Particular preference is given to the polymers composed of more than 60% by weight of C1-C10 alkyl (meth)acrylates, styrene or mixtures thereof.

The polymers may further comprise hydroxyl-functional monomers in keeping with the above hydroxyl group content, and, if desired, further monomers, examples being ethylenically unsaturated acids, especially carboxylic acids, acid anhydrides or acid amides.

Further binders are polyesterols, such as are obtainable by condensing polycarboxylic acids, especially dicarboxylic acids, with polyols, especially diols.
Polyester polyols are known for example from UHmanns Encyklopadie der technischen Chemie, 4th edition, volume 19, pp. 62 to 65. It is preferred to use polyester polyols obtained by reacting dihydric alcohols with dibasic carboxylic acids. In lieu of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or polycarboxylic esters of lower alcohols, or mixtures thereof, to prepare the polyester polyols. The polycarboxylic acids may be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and may be optionally substituted, by halogen atoms for example, and/or unsaturated. Examples thereof that may be mentioned include the following:

10 Oxalic acid, maleic acid, fumaric acid, succinic acid, glutaric acid, adipic acid, sebacic acid, dodecanedioic acid, o-phthalic acid, isophthalic acid, terephthalic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid or tetrahydrophthalic acid, suberic acid, azelaic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydropthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic anhydride, dimeric fatty acids, isomers thereof, hydrogenation products thereof, and esterifiable derivatives thereof, such as anhydrides or dialkyl esters, such as C1-C4 alkyl esters, preferably methyl, ethyl or n-butyl esters, of the stated acids. Preference is given to dicarboxylic acids of the general formula HOOC-(CH2)y-COOH, in which y is a number from 1 to 20, preferably an even number from 2 to 20; particular preference is given to succinic acid, adipic acid, sebacic acid, and dodecanedioic acid.

Suitable polyhydric alcohols for preparing the polyesters include 1,2-propanediol, ethylene glycol, 2,2-dimethyl-1,2-ethanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 3-methylpentane-1,5-diol, 2-ethylhexane-1,3-diol, 2,4-diethyloctane-1,3-diol, 1,6-hexanediol, polyTHF having a molar mass between 162 and 2000, poly-1,3-propanediol having a molar mass between 134 and 898, polyethylene glycol having a molar mass between 106 and 458, neopentyl glycol, neopentyl glycol hydroxyxipivalate, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3-, and 1,4-cyclohexanediethanol, 1,2-, 1,3- or 1,4-cyclohexanediol, trimethylolbutane, trimethylolpropane, trimethylolethane, neopentyl glycol, pentaerythritol, glycerol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol or isomalt, which if desired may be alkoxylated as described above.

Preference is given to alcohols of the general formula HO-(CH2)x-OH, in which x is a number from 1 to 20, preferably an even number from 2 to 20. Preference is given to ethylene glycol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol and dodecane-1,12-diol. Preference is further given to neopentyl glycol.

Also suitable are polycarbonate diols, such as may be obtained, for example, by reacting phosgene with an excess of the low molecular mass alcohols as specified as synthesis components for the polyester polyols.
Also suitable are lactone-based polyester diols, which are homopolymers or copolymers of lactones, preferably hydroxy-terminal products of lactones with suitable difunctional starter molecules. Suitable lactones are preferably those derived from compounds of the general formula \( \text{HO-(CH}_2\text{)}_z\text{-COOH} \), in which \( z \) is a number from 1 to 20 and one hydrogen atom of a methylene unit may also be substituted by a \( \text{C}_1 \) to \( \text{C}_4 \) alkyl radical. Examples are \( \varepsilon \)-caprolactone, \( \beta \)-propiolactone, gamma-butyrolactone and/or methyl- \( \varepsilon \)-caprolactone, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid or pivalolactone, and mixtures thereof. Suitable starter components are, for example, the low molecular mass dihydric alcohols specified above as a synthesis component for the polyester polyols. The corresponding polymers of \( \varepsilon \)-caprolactone are particularly preferred. Lower polyester diols or polyether diols as well can be used as starters for preparing the lactone polymers. In lieu of the polymers of lactones it is also possible to use the corresponding, chemically equivalent polycondensates of the hydroxycarboxylic acids corresponding to the lactones.

Further suitable polymers are polyetherols, which are prepared by addition reaction of ethylene oxide, propylene oxide or butylene oxide with H-active components. Polycondensates of butanediol are suitable as well.

The polymers can of course also be compounds having primary or secondary amino groups.

Suitability is further possessed by polycarbonate polyols, such as may be obtained, for example, by reacting phosgene with an excess of the low molecular mass alcohols specified as synthesis components for the polyester polyols.

Alkyd resins are polycondensation resins made from polyols, polybasic carboxylic acids, and fatty oils, or free natural and/or synthetic fatty acids; at least one polyol must have a functionality of three or more.

As polyols and polybasic carboxylic acids it is possible for example to employ the components specified above in connection with the polyesterols.

Preferred polyhydric alcohols are glycerol, pentaerythritol, trimethylolethane, trimethylolpropane, various diols such as ethane-/propanediol, diethylene glycol, neopentyl glycol.

Preferred polybasic carboxylic acids are phthalic acid (anhydride) (PAA), isophthalic acid, terephthalic acid, trimellitic anhydride, adipic acid, azelaic acid, sebacic acid.

Examples of suitable oil components and/or fatty acids include drying oils, such as linseed oil, oiticica oil or tung oil, semidrying oils, such as soybean oil, sunflower oil, safflower oil, castor oil or tall oil, nondrying oils, such as castor oil, coconut oil or peanut oil, or free fatty acids of above oils, or synthetic monocarboxylic acids.

The molar mass of typical alkyd resins is between 1500 and 20 000, preferably between 3500 and 6000. The acid number is preferably 2 to 30 mg KOH/g, or 35-65-mg KOH/g in the case of...
water-thinnable resins. The OH number is generally up to 300, preferably up to 100 mg KOH/g.

Polyacrylate polyols, polyesterols and/or polyethers of this kind have a molecular weight $M_n$ of preferably at least 1000, more preferably at least 2000, and very preferably at least 5000 g/mol. The molecular weight $M_n$ can be for example up to 200 000, preferably up to 100 000, more preferably up to 80 000, and very preferably up to 50 000 g/mol.

It is also possible to add co-crosslinkers to the coating compositions, examples being trisalkylcarbamoyltriazines (TACT), preferably trismethylcarbamoyltriazines, tris-n-butylcarbamoyltriazines and mixed methylated/n-butylated trisalkylcarbamoyltriazines.

Furthermore, the amino resins of the invention, especially the melamine-formaldehyde resins, may also be used together with noncrosslinkable binders, i.e., those without groups that are reactive toward melamine-formaldehyde resins.

The crosslinking is accelerated by addition of acids and other catalysts.

Weak acids for the purposes of this text are monobasic or polybasic, organic or inorganic, preferably organic, acids having a $pK_a$ of between 1.6 and 5.2, preferably between 1.6 and 3.8.

Examples thereof are carbonic acid, phosphoric acid, formic acid, acetic acid, and maleic acid, glyoxylic acid, bromoacetic acid, chloroacetic acid, thioglycolic acid, glycine, cyanoacetic acid, acrylic acid, malonic acid, hydroxypropanedioic acid, propionic acid, lactic acid, 3-hydroxypropionic acid, glyceric acid, alanine, sarcosine, fumaric acid, acetoacetic acid, succinic acid, isobutyric acid, pentanoic acid, ascorbic acid, citric acid, nitrilotriacetic acid, cyclopentaneacrylic acid, 3-methylglutaric acid, adipic acid, hexanoic acid, benzoic acid, cyclohexanecarboxylic acid, heptanedioic acid, heptanoic acid, phthalic acid, isophthalic acid, terephthalic acid, tolycic acid, phenylacetic acid, phenoxyacetic acid, mandelic acid or sebacic acid.

Preference is given to organic acids, preferably monobasic or polybasic carboxylic acids. Particular preference is given to formic acid, acetic acid, maleic acid or fumaric acid.

Strong acids for the purposes of this text are monobasic or polybasic, organic or inorganic, preferably organic acids having a $pK_a$ of less than 1.6 and more preferably less than 1.

Examples thereof are sulfuric acid, pyrophosphoric acid, sulfurous acid, and tetrafluoroboric acid, trichloroacetic acid, dichloroacetic acid, oxalic acid, and nitroacetic acid.

Preference is given to organic acids, preferably organic sulfonic acids. Particular preference is given to methanesulfonic acid, para-toluenesulfonic acid, benzenesulfonic acid, dodecylbenzenesulfonic acid, cyclododecanesulfonic acid, and camphorsulfonic acid.
The acids are used in amounts in general of up to 10% by weight, preferably 0.1% to 8%, more preferably 0.3% to 6%, very preferably 0.5% to 5%, and in particular from 1% to 3% by weight, based on the amino resin employed.

5 The acids may also be used as free acids or in blocked form.

The (meth)acrylated melamine-formaldehyde resins of the invention may be used as sole binder or, preferably, in combination with at least one further radically polymerizable compound (D).

10 Radically polymerizable groups are, for example, preferably (meth)acrylate groups and more preferably acrylate groups.

The radically polymerizable compounds (D) are preferably polyfunctional (compound having more than one radically polymerizable double bond) polymerizable compounds.

15 (Meth)acrylic acid stands in this specification for methacrylic acid and acrylic acid, preferably for acrylic acid.

Multifunctional polymerizable compounds are preferably multifunctional (meth)acrylates which carry at least 2, preferably 2-10, more preferably 3-6, and very preferably 3-4 (meth)acrylate groups, preferably acrylate groups.

Examples of multifunctional polymerizable compounds are ethylene glycol diacylate, 1,2-propanediol diacylate, 1,3-propanediol diacylate, 1,4-butanediol diacylate, 1,3-butanediol diacylate, 1,5-pentanediol diacylate, 1,6-hexanediol diacylate, 1,8-octanediol diacylate, neopentyl glycol diacylate, 1,1-, 1,2-, 1,3-, and 1,4-cyclohexanediol diacylate, 1,2-, 1,3- or 1,4-cyclohexanediol diacylate, dipropylene glycol diacylate trimethylolpropane triacylate, ditrimethylolpropane tripolyol glycol diacylate penta- or hexaacylate, pentaerythritol tri- or tetraacylate, glycerol di- or triacylate, and also di- and polyacylates of sugar alcohols, such as sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol or isomalt, or of polyester polyols, polyetherols, poly THF having a molar mass of between 162 and 2000, poly-1,3-propanediol having a molar mass of between 134 and 1178, polyethylene glycol having a molar mass of between 106 and 898, and also epoxy tetraacylate dipentaerythritol (meth)acrylates, polyester (meth)acrylates, polyether (meth)acrylates, urethane (meth)acrylates or polycarbonate (meth)acrylates, which optionally may also have been modified with one or more amines.

Further examples are (meth)acrylates of compounds of formula (Va) to (Vd)
in which

\[ R^{13} \text{ and } R^{14} \text{ independently of one another are hydrogen or are C1-C18 alkyl which is optionally substituted by aryl, alkyl, aryloxy, alkyloxy, heteroatoms and/or heterocycles,} \]

\[ a, b, c, \text{ and } d \text{ independently of one another are each an integer from 1 to 10, preferably 1 to 5, and more preferably 1 to 3, and} \]

\[ \text{each } X_i \text{ for } i = 1 \text{ to } k, 1 \text{ to } l, 1 \text{ to } m, \text{ and } 1 \text{ to } q \text{ can be selected independently of one another from the group } -\text{CH2-CH2-O-}, -\text{CH2-CH(CH3)-O-}, -\text{CH(CH3)CH2-0-}, -\text{CH2-C(CH3)2-0-}, -\text{C(CH3)2-CH2-O-}, -\text{CH2-CHVin-0-}, -\text{CHVin-CH2-0-}, -\text{CH2-CHPh-0-}, \text{ and } -\text{CHPh-CH2-0-}, \text{ preferably from the group } -\text{CH2-CH2-0-}, -\text{CH2-CH(CH3)-0-}, \text{ and } -\text{CH(CH3)CH2-0-}, \text{ and more preferably } -\text{CH2-O-}, \]

\[ \text{in which } Ph \text{ is phenyl and Vin is vinyl.} \]

C1-C18 alkyl therein, optionally substituted by aryl, alkyl, aryloxy, alkyloxy, heteroatoms and/or heterocycles, is for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, 1,1-dimethylpropyl, 1,1-dimethybutyl, 1,1,3,3-tetramethylbutyl, preferably methyl, ethyl or n-propyl, more preferably methyl or ethyl.

These are preferably (meth)acrylates of singly to vigintuply and more preferably triply to decuply ethoxylated, propoxylated or mixedly ethoxylated and propoxylated, and in particular exclusively ethoxylated, neopentyl glycol, trimethylolpropane, trimethylolethane or pentaerythritol.
Preferred multifunctional polymerizable compounds are 1,2-propanediol diacrylate, 1,3-propanediol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, trimethylolpropane triacrylate, ditrimethylol tetracrylate, and dipentaerythritol hexaacrylate, polyester polyl acrylates, polyetherol acrylates, and triacrylate of singly to vigintuply alkoxylated, more preferably singly to vigintuply ethoxylated trimethylolpropane, singly to vigintuply propoxylated glycerol or singly to vigintuply ethoxylated and/or propoxylated pentaerythritol.

In one preferred embodiment, epoxy (meth)acrylates are used as multifunctional polymerizable compounds.

Especially preferred multifunctional polymerizable compounds are trimethylolpropane triacrylate and triacrylate of singly to vigintuply ethoxylated trimethylolpropane, triacrylate of singly to vigintuply propoxylated glycerol or tetraacrylate of singly to vigintuply ethoxylated and/or propoxylated pentaerythritol.

Further constituents may also be polyalcohols with full or partial esterification with (meth)acrylic acid.

Examples of such polyalcohols are at least divalent polyols, polyetherols or polyesterols, or polyacrylate polyols, having an average OH functionality of at least 2, preferably at least 3, more preferably at least 4, and very preferably 4 to 20.

Polyetherols, in addition to the alkoxylated polyols, may also be polyethylene glycol having a molar mass of between 106 and 2000, polypropylene glycol having a molar weight of between 134 and 2000, polyTHF having a molar weight of between 162 and 2000, or poly-1,3-propanediol having a molar weight of between 134 and 400.

Polyester polyols are known for example from Ullmanns Encyklopädie der technischen Chemie, 4th edition, volume 19, pp. 62 to 65. Preference is given to using polyester polyols obtained by reacting dihydric alcohols with dibasic carboxylic acids. In lieu of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols or mixtures thereof to prepare the polyester polyols. The polycarboxylic acids may be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and may optionally be substituted, by halogen atoms for example, and/or unsaturated. Examples thereof that may be mentioned include the following:

oxalic acid, maleic acid, fumaric acid, succinic acid, glutaric acid, adipic acid, sebamic acid, dodecanedioic acid, o-phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid or tetrahydrophthalic acid, suberic acid, azelaic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic anhydride, dimeric fatty acids, their isomers and hydrogenation products, and also esterifiable derivatives, such as anhydrides or dialkyl esters, C1-C4-alkyl esters for example,
preferably methyl, ethyl or n-butyl esters, of said acids are used. Preference is given to
dicarboxylic acids of the general formula \( \text{HOOC-(CH}_2\text{)_y-COOH} \), \( y \) being a number from 1 to 20, preferably an even number from 2 to 20; more preferably succinic acid, adipic acid, sebacic acid, and dodecanedicarboxylic acid.

Suitable polyhydric alcohols for preparing the polyesterols include

- 1,2-propanediol, ethylene glycol, 2,2-dimethyl-1,2-ethanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 3-methylpentane-1,5-diol, 2-ethylhexane-1,3-diol, 2,4-diethyl octane-1,3-diol, 1,6-hexanediol, polyethylene glycol having a molar weight between 106 and 2000, polypropylene glycol having a molar weight between 134 and 2000, polyTHF having a molar mass between 162 and 2000, poly-1,3-propanediol having a molar weight between 134 and 400, neopentyl glycol, neopentyl glycol hydroxypivalate, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 2,2-bis(4-hydroxycyclohexyl) propane, 1,1-, 1,2-, 1,3-, and 1,4-cyclohexanediethanol, 1,2-, 1,3- or 1,4-cyclohexanediol, trimethylolbutane, trimethylolpropane, trimethylol ethane, neopentyl glycol, pentaerythritol, glycerol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol or isomalt, which optionally may have been alkoxylated as described above.

Preferred alcohols are those of the general formula \( \text{HO-(CH}_2\text{)}^x\text{OH} \), \( x \) being a number from 1 to 20, preferably an even number from 2 to 20. Preference is given to ethylene glycol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol, and dodecane-1,12-diol. Preference is further given to neopentyl glycol.

Also suitable are lactone-based polyesters diols, which are homopolymers or copolymers of lactones, preferably hydroxyl-terminated adducts of lactones with suitable difunctional starter molecules. Suitable lactones include, preferably, those deriving from compounds of the general formula \( \text{HO-(CH}_2\text{)_z-COOH} \), \( z \) being a number from 1 to 20 and \( z \) being possible for an \( H \) atom of a methylene unit also to have been substituted by a \( \text{Cl} \) to \( \text{C}_4 \) alkyl radical. Examples are \( \varepsilon \)-caprolactone, \( \beta \)-propiolactone, gamma-butyrolactone and/or methyl-\( \varepsilon \)-caprolactone, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid or pivalolactone, and mixtures thereof. Examples of suitable starter components are the low molecular mass dihydric alcohols specified above as a synthesis component for the polyester polyols. The corresponding polymers of \( \varepsilon \)-caprolactone are particularly preferred. Lower polyesters diols or polyether diols as well can be used as starters for preparing the lactone polymers. In lieu of the polymers of lactones it is also possible to use the corresponding, chemically equivalent polycondensates of the hydroxycarboxylic acids corresponding to the lactones.

Also suitable, furthermore, are polycarbonatediols, such as may be obtained, for example, by reacting phosgene with an excess of the low molecular weight alcohols specified as synthesis components for the polyester polyols.

The multifunctional polymerizable compound, may also comprise urethane (meth)acrylates, epoxy (meth)acrylates or carbonate (meth)acrylates.
Urethane (meth)acrylates are obtainable for example by reacting polyisocyanates with hydroxyalkyl (meth)acrylates and optionally chain extenders such as diols, polyols, diamines, polyamines, dithiols or polythiols. Urethane (meth)acrylates which can be dispersed in water without addition of emulsifiers additionally comprise ionic and/or nonionic hydrophilic groups, which are introduced into the urethane by means of synthesis components such as hydroxycarboxylic acids, for example.

Urethane (meth)acrylates of this kind comprise as synthesis components substantially:

1. at least one organic aliphatic, aromatic or cycloaliphatic di- or polyisocyanate,

2. at least one compound having at least one isocyanate-reactive group and at least one radically polymerizable unsaturated group, and

3. optionally, at least one compound having at least two isocyanate-reactive groups.

Possible useful components (1), (2), and (3) may be the same as those described above as synthesis components (a), (b), and (e) for the polyurethanes of the invention.

The urethane (meth)acrylates preferably have a number-average molar weight $M_n$ of 500 to 20 000, in particular of 500 to 10 000 and more preferably 600 to 3000 g/mol (determined by gel permeation chromatography using tetrahydrofuran and polystyrene as standard).

The urethane (meth)acrylates preferably have a (meth)acrylic group content of 1 to 5, more preferably of 2 to 4, mol per 1000 g of urethane (meth)acrylate.

Epoxy (meth)acrylates are obtainable by reacting epoxides with (meth)acrylic acid. Examples of suitable epoxides include epoxidized olefins, aromatic glycidyl ethers or aliphatic glycidyl ethers, preferably those of aromatic or aliphatic glycidyl ethers.

Examples of possible epoxidized olefins include ethylene oxide, propylene oxide, iso-butylene oxide, 1-butene oxide, 2-butene oxide, vinylloxirane, styrene oxide or epichlorohydrin, preference being given to ethylene oxide, propylene oxide, isobutylene oxide, vinylloxirane, styrene oxide or epichlorohydrin, particular preference to ethylene oxide, propylene oxide or epichlorohydrin, and very particular preference to ethylene oxide and epichlorohydrin.

Aromatic glycidyl ethers are, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol B diglycidyl ether, bisphenol S diglycidyl ether, hydroquinone diglycidyl ether, alkylation products of phenol/dicyclopentadiene, e.g., 2,5-bis[(2,3-epoxypropoxy)phenyl]octahydro-4,7-methano-5H-indene (CAS No. [13446-85-0]), tris[4-(2,3-epoxypropoxy)phenyl)methane isomers (CAS No. [66072-39-7]), phenol-based epoxy novolaks (CAS No. [9003-35-4]), and cresol-based epoxy novolaks (CAS No. [37382-79-9]).
Examples of aliphatic glycidyl ethers include 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol tetruglycidyl ether, 1,1,2,2-tetrakis[4-(2,3-epoxypropoxy)phenyl]ethane (CAS No. [27043-37-4]), diglycidyl ether of polypropylene glycol (a,oo-bis[2,3-epoxypropoxy]poly(oxypropylene), CAS No. [16096-30-3]) and of hydrogenated bisphenol A (2,2-bis[4-(2,3-epoxypropoxy)cyclohexyl]propane, CAS No. [13410-58-7]).

The epoxy (meth)acrylates preferably have a number-average molar weight \( M_n \) of 200 to 20 000, more preferably of 200 to 10 000 g/mol, and very preferably of 250 to 3000 g/mol; the amount of (meth)acrylic groups is preferably 1 to 5, more preferably 2 to 4, per 1000 g of epoxy (meth)acrylate (determined by gel permeation chromatography using polystyrene as standard and tetrahydrofuran as eluent).

Carbonate (meth)acrylates comprise on average preferably 1 to 5, especially 2 to 4, more preferably 2 to 3 (meth)acrylic groups, and very preferably 2 (meth)acrylic groups.

The number-average molecular weight \( M_n \) of the carbonate (meth)acrylates is preferably less than 3000 g/mol, more preferably less than 1500 g/mol, very preferably less than 800 g/mol (determined by gel permeation chromatography using polystyrene as standard, tetrahydrofuran as solvent).

The carbonate (meth)acrylates are obtainable in a simple manner by transesterifying carbonic esters with polyhydric, preferably dihydric, alcohols (diols, hexanediol for example) and subsequently esterifying the free OH groups with (meth)acrylic acid, or else by transesterification with (meth)acrylic esters, as described for example in EP-A 92 269. They are also obtainable by reacting phosgene, urea derivatives with polyhydric, e.g., dihydric, alcohols.

Also conceivable are (meth)acrylates of polycarbonate polyols, such as the reaction product of one of the aforementioned diols or polyols and a carbonic ester and also a hydroxyl-containing (meth)acrylate.

Examples of suitable carbonic esters include ethylene carbonate, 1,2- or 1,3-propylene carbonate, dimethyl carbonate, diethyl carbonate or dibutyl carbonate.

Examples of suitable hydroxyl-containing (meth)acrylates are 2-hydroxyethyl (meth)acrylate, 2- or 3-hydroxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, glyceryl mono- and di(meth)acrylate, trimethylolpropane mono- and di(meth)acrylate, and pentaerythritol mono-, di-, and tri(meth)acrylate.

Particularly preferred carbonate (meth)acrylates are those of the formula:
in which R is H or CH₃, X is a C₂-C₁₈ alkylene group, and n is an integer from 1 to 5, preferably 1 to 3.

R is preferably H and X is preferably C₂ to C₁₀ alkylene, examples being 1,2-ethylene, 1,2-propylene, 1,3-propylene, 1,4-butylene, and 1,6-hexylene, more preferably C₄ to C₆ alkylene. With very particular preference X is C₆ alkylene.

The carbonate (meth)acrylates are preferably aliphatic carbonate (meth)acrylates.

Among the multifunctional polymerizable compounds, compounds of formula (Va) to (Vd) are particularly preferred.

It may be useful to add photoinitiator to the coating composition of the invention.

Photoinitiators (E) may be, for example, photoinitiators known to the skilled person, examples being those specified in "Advances in Polymer Science", Volume 14, Springer Berlin 1974 or in K. K. Dietliker, Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints, Volume 3; Photoinitiators for Free Radical and Cationic Polymerization, P. K. T. Oldring (Eds), SITA Technology Ltd, London.

Suitability is possessed, for example, by mono- or bisacylphosphine oxides, as described for example in EP-A 7 508, EP-A 57 474, DE-A 196 18 720, EP-A 495 751 or EP-A 615 980, examples being 2,4,6-trimethylbenzozyldiphenylphosphine oxide (Lucirin® TPO from BASF SE), ethyl 2,4,6-trimethylbenzoylphenylphosphinate (Lucirin® TPO L from BASF SE), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure® 819 from BASF SE), benzophenones, hydroxyacetophenones, phenylglyoxylic acid and its derivatives, or mixtures of these photoinitiators. Examples that may be mentioned include benzophenone, acetonaphthoquinone, acetonaphthoquinone, methyl ethyl ketone, valerophenone, hexanophenone, ophenylbutyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, β-methylantraquinine, tert-butylantraquinine, anthraquinonecarboxylic esters, benzaldehyde, otetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthone, 3-acetylphenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,4-triacetylbenzene, thioxanthen-9-one, xanthen-9-one, 2,4-dimethylthioxanthone, 2,4-dimethylthioxanthone, 2,4-dimethylthioxanthone, 2,4-dichlorothioxanthone, benzoin, benzoin isobutyl ether, chloroxanthone, benzoin tetrahydropranyl ether, benzoin methyl ether, benzoin ethyl ether, benzoin butyl ether, benzoin isopropyl ether, 7H-benzoin methyl ether, benz[de]anthracen-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino)benzophenone, 4-phenylbenzophenone, 4-chlorobenzophenone, Michler's ketone, 1-acetonaphthone, 2-acetonaphthone, 1-benzoyl-
cyclohexan-1-ol, 2-hydroxy-2,2-dimethylacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, 1-hydroxyacetophenone, acetophenone dimethyl ketal, o-methoxybenzophenone, 2-hydroxy-1-[4-[(2-hydroxy-2-methylpropanoyl)phenyl][methyl][phenyl]-2-methylpropan-1-one, 2-benzyl-2-dimethylamino-4'-morp-holinobutyrophenone, 2-(dimethylamino)-1-(4-morpholinophenyl)-2-(p-tolylimethyl)butan-1-one, 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one, 2-triphenylphosphine, tri-o-tolyolphosphate, benz[a]anthracene-7,12-dione, 2,2-diethoxyacetophenone, benzil ketals, such as benzil dimethyl ketal, anthraquinones such as 2-methylantraquinone, 2-ethylanthraquinone, 2-tert-butylantraquinone, 1-chloroantraquinone, and 2-amylantraquinone, and 2,3-butanedione.

Likewise conceivable as photoinitiators are polymeric photoinitiators such as, for example, the diester of carboxymethoxybenzophenone with polytetramethylene glycols of different molar weights, preferably 200 to 250 g/mol (CAS 515136-48-8), and also CAS 1246194-73-9, CAS 813452-37-8, CAS 71512-90-8, CAS 886463-10-1, or further polymeric benzophenone derivatives, of the kind available commercially, for example, under the trade name Omnipol® BP from IGM Resins B.V., Waalwijk, The Netherlands, or Genopol® BP1 from Rahn AG, Switzerland. Also conceivable, furthermore, are polymeric thioxanthenes, examples being the diesters of carboxymethoxythioxanthenes with polytetramethylene glycols of various molar weights, of the kind available commercially, for example, under the trade name Omnipol® TX from IGM Resins B.V., Waalwijk, The Netherlands. Also conceivable, furthermore, are polymeric amino ketones, examples being the diester of carboxyethoxythioxanthenes with polyethylene glycols of various molar weights, of the kind available commercially, for example, under the trade name Omnipol® 910 or Omnipol® 9210 from IGM Resins B.V., Waalwijk, The Netherlands.

One preferred embodiment uses, as photoinitiators, silsesquioxane compounds having at least one initiating group, of the kind described in WO 2010/063612 A1, particularly from page 2, line 21 to page 43, line 9 therein, hereby incorporated by reference as part of the present disclosure content, preferably from page 2, line 21 to page 30, line 5, and also the compounds described in the examples of WO 2010/063612 A1.

Also suitable are nonyellowing or low-yellowing photoinitiators of the phenylglyoxalic ester type, as described in DE-A 198 26 712, DE-A 199 13 353 or WO 98/33761, and silsesquioxane compounds.

Preference among these photoinitiators is given to 2,4,6-trimethylbenzoyldiphenylphosphine oxide, ethyl 2,4,6-trimethylbenzoylphenylphosphinate, bis(2,4,6-trimethylbenzoyl)phenylphos-phine oxide, 2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone, 2-(dimethylamino)-1-(4-morpholinophenyl)-2-(p-tolylimethyl)butan-1-one, 2-hydroxy-1-[4-[(2-hydroxy-2-methylpro-panoyl)phenyl][methyl][phenyl]-2-methylpropan-1-one, and also the above-described polymeric thioxanthone and benzophenone derivatives, and also those described in WO 2010/063612 A1.

Pigments (F) may likewise be comprised. Pigments, according to CD Rompp Chemie Lexikon - Version 1.0, Stuttgart/New York: Georg Thieme Verlag 1995, with reference to DIN 55943, are
particulate, organic or inorganic, chromatic or achromatic colorants which are virtually insoluble in the application medium.

Virtually insoluble here means a solubility at 25°C of below 1 g / 1000 g of application medium, preferably below 0.5 g, more preferably below 0.25 g, very preferably below 0.1 g, and in particular below 0.05 g / 1000 g of application medium.

Examples of pigments comprise any desired systems of absorption pigments and/or effect pigments, preferably absorption pigments. There are no restrictions whatsoever governing the number and selection of the pigment components. They can be adapted as desired to the particular requirements, such as the desired color impression, for example. By effect pigments are meant all pigments which exhibit a platelet-shaped construction and impart specific decorative color effects to a surface coating. The effect pigments comprise, for example, all of the effect-imparting pigments which can be employed commonly in vehicle finishing and industrial coating. Examples of effect pigments of this kind are pure metal pigments, such as aluminum, iron or copper pigments; interference pigments, such as titanium-dioxide-coated mica, iron-oxide-coated mica, mixed-oxide-coated mica (e.g., with titanium dioxide and Fe₂O₃) or titanium dioxide and Cr₂O₃, metal-oxide-coated aluminum, and liquid-crystal pigments.

The color-imparting absorption pigments are, for example, customary organic or inorganic absorption pigments which can be used in the coatings industry. Examples of organic absorption pigments are azo pigments, phthalocyanine pigments, quinacridone pigments, and pyrrolopyrrole pigments. Examples of inorganic absorption pigments are iron oxide pigments, titanium dioxide, and carbon black.

Recited below are examples of particularly suitable pigments.

Organic pigments:

- Monoazo pigments: C.I. Pigment Brown 25; C.I. Pigment Orange 5, 13, 36 and 67; C.I. Pigment Red 1, 2, 13, 3, 5, 8, 9, 12, 17, 22, 23, 31, 48:1, 48:2, 48:3, 48:4, 49, 49:1, 52:1, 52:2, 53, 53:1, 53:3, 57:1, 63, 112, 146, 170, 184, 210, 245 and 251; C.I. Pigment Yellow 1, 3, 73, 74, 65, 97, 151 and 183;

- Disazo pigments: C.I. Pigment Orange 16, 34 and 44; C.I. Pigment Red 144, 166, 214 and 242; C.I. Pigment Yellow 12, 13, 14, 16, 17, 81, 83, 106, 113, 126, 127, 155, 174, 176 and 188;

- Anthanthrone pigments: C.I. Pigment Red 168 (C.I. Vat Orange 3);
- Anthraquinone pigments: C.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;
- Anthraquinone pigments: C.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;
- Anthropyrimidine pigments: C.I. Pigment Yellow 108 (C.I. Vat Yellow 20);
- Quinacridone pigments: C.I. Pigment Red 122, 202 and 206; C.I. Pigment Violet 19;
Quinophthalone pigments: C.I. Pigment Yellow 138;
- Dioxazine pigments: C.I. Pigment Violet 23 and 37;
- Flavanthrone pigments: C.I. Pigment Yellow 24 (C.I. Vat Yellow 1);
- Indanthrone pigments: C.I. Pigment Blue 60 (C.I. Vat Blue 4) and 64 (C.I. Vat Blue 6);
- Isoindoline pigments: C.I. Pigment Orange 69; C.I. Pigment Red 260; C.I. Pigment Yellow 139 and 185;
- Isoindolinone pigments: C.I. Pigment Orange 61; C.I. Pigment Red 257 and 260; C.I. Pigment Yellow 109, 110, 173 and 185;
- Isoviolanthrone pigments: C.I. Pigment Violet 31 (C.I. Vat Violet 1);
- Perinone pigments: C.I. Pigment Orange 43 (C.I. Vat Orange 7); C.I. Pigment Red 194 (C.I. Vat Red 15);
- Perylene pigments: C.I. Pigment Black 31 and 32; C.I. Pigment Red 123, 149, 178, 179 (C.I. Vat Red 23), 190 (C.I. Vat Red 29) and 224; C.I. Pigment Violet 29;
- Phthalocyanine pigments: C.I. Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6 and 16; C.I. Pigment Green 7 and 36;
- Pyranthrone pigments: C.I. Pigment Orange 51; C.I. Pigment Red 216 (C.I. Vat Orange 4);
- Triarylcyanine pigments: C.I. Pigment Red 88 and 181 (C.I. Vat Red 1); C.I. Pigment Violet 38 (C.I. Vat Violet 3);
- Triarylcarbonium pigments: C.I. Pigment Blue 1, 61 and 62; C.I. Pigment Green 1; C.I. Pigment Red 81, 81:1 and 169; C.I. Pigment Violet 1, 2, 3 and 27; C.I. Pigment Black 1 (aniline black);

C.I. Pigment Yellow 101 (aldazine yellow); C.I. Pigment Brown 22.

Inorganic pigments:
- White pigments: titanium dioxide (C.I. Pigment White 6), zinc white, pigmented zinc oxide, barium sulfate, zinc sulfide, lithopones; lead white; calcium carbonate;

- Black pigments: iron oxide black (C.I. Pigment Black 11), iron-manganese black, spinel black (C.I. Pigment Black 27); carbon black (C.I. Pigment Black 7);

- Color pigments: chromium oxide, chromium oxide hydrate green; chromium green (C.I. Pigment Green 48); cobalt green (C.I. Pigment Green 50); ultramarine green; cobalt blue (C.I. Pigment Blue 28 and 36); ultramarine blue; iron blue (C.I. Pigment Blue 27); manganese blue; ultramarine violet; cobalt and manganese violet; iron oxide red (C.I. Pigment Red 101); cadmium sulfoselenide (C.I. Pigment Red 108); molybdate red (C.I. Pigment Red 104); ultramarine red;
Iron oxide brown, mixed brown, spinel and corundum phases (C.I. Pigment Brown 24, 29 and 31), chromium orange;

Iron oxide yellow (C.I. Pigment Yellow 42); nickel titanium yellow (C.I. Pigment Yellow 53; C.I. Pigment Yellow 157 and 164); chromium titanium yellow; cadmium sulfide and cadmium zinc sulfide (C.I. Pigment Yellow 37 and 35); chromium yellow (C.I. Pigment Yellow 34), zinc yellow, alkaline earth metal chromates; Naples yellow; bismuth vanadate (C.I. Pigment Yellow 184);

- Interference pigments: metallic effect pigments based on coated metal platelets;
  pearlescent pigments based on metal oxide coated mica platelets; liquid crystal pigments.

Preferred pigments (F) in this context are monoazo pigments (especially laked BONS pigments, Naphthol AS pigments), disazo pigments (especially diaryl yellow pigments, bisacetoacetoanilide pigments, disazopyrazolone pigments), quinacridone pigments, quinophthalone pigments, perinone pigments, phthalocyanine pigments, triarylcarbonium pigments (alkali blue pigments, laked rhodamines, dye salts with complex anions), isoindoline pigments, white pigments, and carbon blacks.

Examples of particularly preferred pigments (B) are specifically: carbon black, titanium dioxide, C.I. Pigment Yellow 138, C.I. Pigment Red 122 and 146, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3 and 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 5, 38 and 43 and C.I. Pigment Green 7.

Examples of further, typical coatings additives (G) used can be antioxidants, stabilizers, activators (accelerants), fillers, pigments, dyes, antistatic agents, flame retardants, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers or chelating agents.

Suitable thickeners, in addition to free-radically (co)polymerized (co)polymers, include customary organic and inorganic thickeners such as hydroxyethylcellulose or bentonite.

Chelating agents which can be used include, for example, ethylenediamineacetic acid and its salts, and also β-diketones.

Suitable fillers comprise silicates, examples being silicates obtainable by silicon tetrachloride hydrolysis, such as Aerosil® from Evonik, siliceous earth, talc, aluminum silicates, magnesium silicates, calcium carbonates, etc.

Suitable stabilizers comprise typical UV absorbers such as oxaniilides, triazines, and benzotriazoles (the latter available as Tinuvin® grades from BASF), and benzophenones. They can be used alone or together with suitable free-radical scavengers, examples being sterically hindered amines such as 2,2,6,6-tetramethylpiperidine, 2,6-di-tert-butylpiperidine or derivatives thereof, e.g., bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate. Stabilizers are used usually in amounts of 0.1% to 5.0% by weight, based on the solid components comprised in the
The coating materials may be applied one or more times by any of a very wide variety of spraying methods, such as compressed-air, airless or electrostatic spraying methods, using one- or two-component spraying units, or else by injecting, troweling, knifecoating, brushing, rolling, roller coating, pouring, laminating, injection backmolding or coextruding.

The coating thickness is generally in a range from about 3 to 1000 g/m² and preferably 10 to 200 g/m².

Curing is generally accomplished by drying the coatings with the coating compositions or formulations comprising the amino resins of the invention, optionally admixed with further, typical coatings additives and thermally curable resins, preferably at a temperature below 80°C, preferably room temperature to 60°C, and more preferably room temperature to 40°C, for a time of 1 minute and not more than 72 hours, preferably of not more than 48 hours, more preferably of not more than 24 hours, very preferably of not more than 12 hours, and in particular of not more than 6 hours, and subjecting them to thermal treatment (curing) under an oxygen-containing atmosphere, preferably air, or under inert gas at temperatures between 80 and 270°C, preferably between 100 and 240°C, and more preferably between 120 and 180°C. In the drying operation, preferably at least 25%, more preferably at least 50%, and very preferably at least 60%, by weight, of the solvent present in the coating composition prior to application ought to be removed from the applied coating material. Curing of the coating takes place, as a function of the amount of coating material applied, via high-energy radiation, heat transfer from heated surfaces, or via convection of gaseous media, over a period of from seconds, for example, in the case of coil coating in combination with NIR drying, up to 5 hours, for example, high-build systems on temperature-sensitive materials, usually not less than 10 minutes, preferably not less than 15 minutes, more preferably not less than 30 minutes, and very preferably not less than 45 minutes. Drying essentially comprises removal of existing solvent, and in addition there may also even at this stage be reaction with the binder, whereas curing essentially comprises reaction with the binder.

Instead of or in addition to thermal curing, curing may also take place by means of IR and NIR radiation, with NIR radiation here denoting electromagnetic radiation in the wavelength range from 760 nm to 2.5 μm, preferably from 900 to 1500 nm.

Curing takes place in a time of 1 second to 120 minutes, preferably of 1 minute to 60 minutes.

Additionally disclosed is a method of coating substrates which involves applying the coating composition of the invention or paint formulations comprising it, optionally admixed with thermally curable resins, to the substrate, drying it, and then curing it with electron beams or UV exposure under an oxygen-containing atmosphere or, preferably, under inert gas, optionally at temperatures up to the level of the drying temperature.

The method of coating substrates can also be practiced by irradiating the applied coating composition of the invention, or paint formulations, first with electron beams or UV exposure, under
oxygen or, preferably, under inert gas, in order to obtain preliminary curing, then carrying out thermal treatment at temperatures up to 160°C, preferably between 60 and 160°C, and subsequently completely curing with electron beams or UV exposure under oxygen or, preferably, under inert gas.

If a plurality of layers of the coating material are applied one on top of another, drying and/or radiation curing may optionally take place after each coating operation.

Examples of suitable radiation sources for the radiation cure are low-pressure, medium-pressure, and high-pressure mercury lamps, and also fluorescent tubes, pulsed lamps, metal halide lamps, electronic flash devices, which allow radiation curing without a photoinitiator, or excimer lamps. The radiation cure is accomplished by exposure to high-energy radiation, i.e., UV radiation or daylight, preferably light emitted in the wavelength range of $\lambda=200$ to 700 nm, more preferably $\lambda=200$ to 500 nm, and very preferably $\lambda=250$ to 400 nm, or by irradiation with high-energy electrons (electron radiation; 150 to 300 keV). Examples of radiation sources used include high-pressure mercury vapor lamps, lasers, pulsed lamps (flash light), halogen lamps or excimer lamps. The radiation dose typically sufficient for crosslinking in the case of UV curing is situated in the range from 80 to 3000 mJ/cm$^2$.

It will be appreciated that it is also possible to use two or more radiation sources for the cure, two to four for example.

These sources may also each emit in different wavelength ranges.

Drying and/or thermal treatment may also take place, in addition to or instead of the thermal treatment, by means of NIR radiation, which here refers to electromagnetic radiation in the wavelength range from 760 nm to 2.5 $\mu$m, preferably from 900 to 1500 nm.

Irradiation can optionally also be carried out in the absence of oxygen, such as under an inert gas atmosphere. Suitable inert gases are preferably nitrogen, noble gases, carbon dioxide, or combustion gases. Furthermore, irradiation may take place with the coating composition being covered with transparent media. Examples of transparent media are polymeric films, glass or liquids, water for example. Particular preference is given to irradiation in the manner described in DE-A1 199 57 900.

Examples of suitable substrates for the coating compositions of the invention include thermoplastic polymers, particularly polymethyl methacrylates, polybutyl methacrylates, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, acrylonitrile-ethylene-propylene-diene-styrene copolymers (A-EPDM), polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

Mention may further be made of polyethylene, polypropylene, polystyrene, polybutadiene, polyesters, polyamides, polyethers, polycarbonate, polyvinylacetals, polyacrylonitrile, polyacetal,
polyvinyl alcohol, polyvinyl acetate, phenolic resins, urea resins, melamine resins, alkyd resins, epoxy resins or polyurethanes, block or graft copolymers thereof, and blends of these.

Mention may preferably be made of ABS, AES, AMMA, ASA, EP, EPS, EVA, EVAL, HDPE, LDPE, MABS, MBS, MF, PA, PA66, PAN, PB, PBT, PBTP, PC, PE, PEC, PEEK, PEI, PEK, PEP, PES, PET, PETP, PF, PI, PIB, PMMA, POM, PP, PPS, PS, PSU, PUR, PVAC, PVAL, PVC, PVDC, PVP, SAN, SB, SMS, UF, UP plastics (abbreviated names in accordance with DIN 7728), and aliphatic polyketones.

Particularly preferred substrates are glass and metals, which, if desired, may have been pretreated with a primer.

As far as the type of metal is concerned, suitable metals may in principle be any desired metals. In particular, however, they are metals or alloys of the kind customarily employed as metallic materials of construction, requiring protection against corrosion.

The surfaces in question are in particular those of iron, steel, Zn, Zn alloys, Al or Al alloys. These are the surfaces of elements composed entirely of the metals or alloys in question. Alternatively, the elements may have been only coated with these metals and may themselves be composed of materials of other kinds, such as other metals, alloys, polymers or composite materials. They may be the surfaces of castings made from galvanized iron or steel. In one preferred embodiment of the present invention the surfaces are steel surfaces.

Zn alloys or Al alloys are known to the skilled worker. The skilled worker selects the nature and amount of alloying constituents in accordance with the desired end-use application. Typical constituents of zinc alloys comprise, in particular, Al, Pb, Si, Mg, Sn, Cu or Cd. Typical constituents of aluminum alloys comprise, in particular, Mg, Mn, Si, Zn, Cr, Zr, Cu or Ti. The alloys may also be Al/Zn alloys in which Al and Zn are present in an approximately equal amount. Steel coated with alloys of these kinds is available commercially. The steel may comprise the customary alloying components known to the skilled worker.

Also conceivable is the use of the coating compositions of the invention for treating tin-plated iron/steel (tinplate).

The coating compositions and formulations of the invention are additionally suitable for coating substrates such as wood, paper, textile, leather, nonwoven, plastics surfaces, glass, ceramic, mineral building materials, such as cement moldings and fiber-cement slabs, or coated or uncoated metals, preferably plastics or metals, particularly in the form of sheets, more preferably metals.

The amino resins, coating compositions or coating formulations of the invention are suitable as or in exterior coatings, i.e., applications where they are exposed to daylight, preferably parts of buildings, interior coatings, and coatings on vehicles and aircraft. In particular the amino resins and coating compositions of the invention are used as or in automotive clearcoat and topcoat
material(s). Further preferred applications are in can coating and coil coating.

They are particularly suitable for use as primers, surfacers, pigmented topcoat materials, and clearcoat materials in the segments of industrial, wood, automotive, especially OEM, finishing, or decorative coating. The coating compositions are especially suitable for applications where there is a need for particularly high application reliability, external weathering resistance, optical qualities, solvent resistance and/or chemical resistance.

The examples which follow are intended to illustrate the properties of the invention but without restricting it.

Examples

Parts in this text, unless indicated otherwise, are by weight.

Luwipal® 066LF from BASF SE is a highly to fully methyl-etherified melamine-formaldehyde resin having a nonvolatiles content (as per ISO 3251) of 93-96% by weight, with a low free formaldehyde content of not more than 0.3% by weight. The viscosity (ISO 3219 B) is 2.0-6.0 Pas at 23°C and a shear rate D of 4.13 s⁻¹.

Example 1

The thoroughly mixed initial charge of 518.8 g of acrylic acid, 4.05 g of methylhydroquinone, 2.03 g Kerobit and, 0.02 g of phenothiazine was admixed at room temperature with 0.936 g of p-toluene sulfonic acid. Heating took place up to an internal temperature of 95°C.

156.18 g of Luwipal 66 dissolved in 250 ml methylcyclohexane was added within 70 minutes, the internal temperature was raised to 105.9 °C.

Over 9 hours methanol was distilled off, afterwards the reaction was stopped and the reaction mixture was concentrated in vacuo.

After the end of reaction, a highly viscous product was obtained having an acid number of 134 mg KOH/g and a molecular weight Mn of 1661 g/mol. The substitution pattern was measured by NMR to be 4.5 acrylic groups per melamine core.

Use in UV-curable coatings

A formulation of the product from example 1 was mixed with Irgacure® 500 (BASF SE) and applied to a substrate using a four-path frame-type wet film applicator with a gap depth of 100 μm. The film was exposed with 1900 mJ/cm² (high-pressure Hg lamp) at room temperature in a nitrogen atmosphere. Cured film:

Pendulum damping: 205 sec

Use in acid-curable coatings
A formulation of the product from example 1 was mixed with Nacure® 2500 and applied to a substrate using a four-path frame-type wet film applicator with a gap depth of 100 μη. The film was cured at 120 °C for 2 hours. Cured film:

Pendulum damping: 197.5 sec

Example 2

The thoroughly mixed initial charge of 129.7 g of acrylic acid, 0.51 g of methylhydroquinone, 0.25 g Kerobit and, 0.005 g of phenothiazine was admixed at room temperature with 0.234 g of p-toluene sulfonic acid. Heating took place up to an internal temperature of 95°C. 39.04 g of Luwipal 66 dissolved in 250 ml toluene was added within 45 minutes, the internal temperature was raised to 104.5 °C.

Over 7 hours methanol was distilled off, afterwards the reaction was stopped and the reaction mixture was concentrated in vacuo.

After the end of reaction, 65.3 g of a highly viscous product was obtained having an acid number of 139 mg KOH/g.

Example 3

The thoroughly mixed initial charge of 129.7 g of acrylic acid, 0.51 g of methylhydroquinone, 0.17 g Kerobit and, 0.005 g of phenothiazine was admixed at room temperature with 0.234 g of p-toluene sulfonic acid. Heating took place up to an internal temperature of 95°C. 39.04 g of Luwipal 66 dissolved in 250 ml methylcyclohexane was added within 45 minutes, the internal temperature was raised to 102.5 °C.

Over 6 hours methanol was distilled off, afterwards the reaction was stopped and the reaction mixture was concentrated in vacuo.

After the end of reaction, a highly viscous product was obtained having an acid number of 195 mg KOH/g.
Claims

1. Process for the preparation of (meth)acrylated melamine-formaldehyde resins, wherein at least one at least one partially methylolated melamine-formaldehyde resin of formula (I)

\[
\begin{align*}
\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5 \text{and } \text{R}^6 \text{ are each independently of another a } \text{Ci}^{-} \text{ to } \text{Ci2}-\text{alkyl radical and} \\
\text{k, m, n, o, p and q are each independently of another a positive integer of 1 to 10} \\
\text{is reacted with (meth)acrylic acid in the presence of at least one acid (B) yielding a (meth)acrylated melamine-formaldehyde resin of formula (II)}
\end{align*}
\]
wherein

$$R^7, R^8, R^9, R^{10}, R^{11} \text{ and } R^{12}$$ are each independently of another a \text{Ci- to Ci2-alkyl residue or}
a (meth)acryloyl group and

$$r, s, t, u, v, \text{ and } w$$ are each independently of another 0 (zero) or a positive integer of 1 to 10,

wherein at least one of $$r, s, t, u, v, \text{ and } w$$ is > 0 (zero),

with the proviso that at least three of the radicals $$R^7$$ to $$R^{12}$$ are (meth)acryloyl group.

2. Process according to Claim 1, wherein $$R^1, R^2, R^3, R^4, R^5$$ and $$R^6$$ are independently of each other selected from the group consisting of methyl, ethyl, isobutyl and n-butyl.

3. Process for the preparation of (meth)acrylated benzoguanamine-formaldehyde resins,

wherein at least one at least one partially methylolated benzoguanamine-formaldehyde resin of formula (III)

$$\begin{array}{c}
\text{R}^1 \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{R}^2 \quad \text{O} \\
\text{N} \quad \text{N} \\
\text{R}^3 \quad \text{O} \\
\text{O} \quad \text{R}^4 \\
\end{array}$$

wherein

$$R^1, R^2, R^3, \text{ and } R^4$$ are each independently of another a \text{Ci- to Ci2-alkyl radical and}

$$k, m, n, o, p \text{ and } q$$ are each independently of another a positive integer of 1 to 10

is reacted with (meth)acrylic acid in the presence of at least one acid (B) yielding a

(meth)acrylated benzoguanamine-formaldehyde resin of formula (IV)
wherein

5 \( \text{R}^7, \text{R}^8, \text{R}^9, \) and \( \text{R}^{10} \) are each independently of another a \( \text{C}1-\text{C}2 \)-alkyl residue or a (meth)acryloyl group and

10 r, s, t, and u are each independently of another 0 (zero) or a positive integer of 1 to 10, wherein at least one of r, s, t, and u is > 0 (zero), with the proviso that at least two of the radicals \( \text{R}^7 \) to \( \text{R}^{10} \) are (meth)acryloyl group.

4. Process according to any of the preceding claims, wherein the acid (B) exhibits a pKa-value of 3 or less.

5. Process according to any of the preceding claims, wherein the acid (B) is selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, para-toluenesulfonic acid, benzenesulfonic acid, dodecylbenzenesulfonic acid, methanesulfonic acid, nonylnaphthalenedisulfonic acid and mixtures thereof.

6. Process according to any of the preceding claims, wherein the reaction occurs at a temperature of 40 to 120 for 10 minutes to 6 hours, wherein (meth)acrylic acid is used in a ratio of 1:1 to 20:1 (molar) with respect to amino resin.

7. (Meth)acrylated melamine-formaldehyde resin of formula (II)
wherein

R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> und R<sub>12</sub> are each independently of another a Ci- to Ci2-alkyl residue or a (meth)acryloyl group and

r, s, t, u, v, and w are each independently of another 0 (zero) or a positive integer of 1 to 10,

wherein at least one of r, s, t, u, v, and w is > 0 (zero),

with the proviso that at least three of the radicals R<sub>7</sub> to R<sub>12</sub> are (meth)acryloyl group.

8. Coating composition, comprising
- at least one (meth)acrylated melamine-formaldehyde resin according to Claim 7,
- at least one binder (C), comprising groups that are reactive towards amino resins,
- optional at least one radiation curable compound (D),
- at least one photoinitiator (E) and /or 0.1 to 10 % by weight of an acid,
- optional at least one pigment (F), and
- optional at least one typical coating additive (G).

9. Use of (meth)acrylated melamine-formaldehyde resin according to Claim 7 in radiation curable coating compositions.

10. A method of coating substrates which involves applying the coating composition according to Claim 8, optionally admixed with thermally curable resins, to the substrate, drying it, and then curing it with electron beams or UV exposure under an oxygen-containing atmosphere or, preferably, under inert gas, optionally at temperatures up to the level of the drying temperature.